Survey of the Distribution and Sources of PAHs in Urban Surface Soils

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Abstract

It has long been recognized that urban surface soils contain various amounts of polycyclic aromatic hydrocarbons (PAHs). Several studies in the U.S. and Europe have indicated that the concentrations of PAHs in urban surface soils can range from the low parts per billion to hundreds of parts per million depending on the proximity to and contribution from PAH sources. However, the nature and distribution of PAH concentrations in urban surface soil is not well defined because of the lack of a comprehensive, high quality data base.

This paper presents the results of two studies of PAHs in urban surface soil. Surface soil samples from over 300 sites in 26 population centers in three states were collected and analyzed for PAHs. Site selection was conducted using a pseudo-random sampling scheme. The samples were collected from 0 to 15.2 cm (0 to 6 inches). At some locations, samples were collected from two depths, 0 - 2.54 cm and 2.54 – 15.2 cm. The samples were analyzed for 40 PAHs and alkylated PAHs by GC/MS. The results showed that PAHs in surface soils are log-normally distributed. The concentrations of total PAHs ranged from 0.2 mg/kg to 130 mg/kg with an average concentration of 10 mg/kg total PAHs and a median concentration of 4 mg/kg. All 40 PAHs were detectable in most samples above a detection limit of 0.005 mg/kg; however, PAH concentrations were dominated by a few high molecular weight parent compounds. EPA residential risk based concentrations (RBCs) were exceeded for one or more compounds in more than 50 % of the samples tested. The data from this study were compared to similar studies conducted by the City of Chicago and the Massachusetts Department of Environmental Protection.

Background

The natural and human-related sources of polycyclic aromatic hydrocarbons (PAHs) to the environment are numerous and diverse. They include, but are not limited to: volcanic eruptions, forest fires, cigarette smoke, vehicular emissions, and industrial processes. As a result of their many sources and pathways to various environmental media, PAHs are considered ubiquitous. They have been found in air, soil, dust, and sediment samples, even in areas regarded as pristine or not known to be directly impacted by human activities (Blumer 1976).

Although there are many literature references concerning the presence of PAHs in environmental media, including surface soils, a review of those references has indicated that there is a lack of quality research concerning the distributions and concentrations of PAHs in surface soils. In addition, the definition of "surface" soils varies from reference to reference with no general consistency in the depths at which samples were collected. Consequently, compiling and comparing literature data on background PAHs in surface soils is extremely difficult.

The frequent detection of PAHs in surface soil and sediment is of particular importance for environmental investigations and cleanups, because the concentrations of PAHs often define the extent of contamination and the estimated risk from contamination at a variety of sites.

This paper summarizes work designed to generate an internally consistent, rugged set of PAH concentrations in surface soils from a statistically significant number of locations in populated areas above a set size and population density. The samples were collected and analyzed so that PAH data collected at different times and from different locations would be comparable, and would not contain unacceptable sampling or analytical bias.

Methods and Materials

Definitions

Sample Location - the actual place where an individual sample was collected. Each sample location corresponds with the sample identification number on its sample jar and on the chain-of-custody form.

Site - the property or plot of land containing one or more sample locations. For example, "Chestnut Hill Park" or "highway 1 median" was designated as the "site".

Area - A city, town, county, or other locality that may contain multiple sites.

Urbanized Area (UA) - an area consisting of a central place and adjacent urban fringe that together have a minimum residential population of at least 50,000 people and an overall population density of 1,000 people per square mile of land area (U.S. Census Bureau, 2000).

Populated Area - an area that has a population density of 1,000 people per square mile of land area (equivalent to the UA), but with a minimum residential population of 10,000 people. The populated area designation includes smaller cities and towns that have significant urban centers, but do not meet the U.S. Census Bureau's definition of an urbanized area.

Study Area

Because the objective of the study was to examine the distribution of PAHs in urban soils, potential sampling sites were constrained to areas with a minimum population density. The United States Census Bureau defines an urban area as having a minimum of 50,000 persons in a density of greater than 1000 persons per square mile. However, this definition would eliminate from consideration many small to medium-sized cities and towns with substantial commercial and industrial histories. Therefore, a project-specific limit, called a Populated Area, was used that included any area with greater than 10,000 persons and a density of >1000 persons/sq. mi. This included most of the smaller urban centers.

Samples were collected from four populated areas in New York State, 16 populated areas in Illinois, and 6 populated areas in a western state. The specific populated areas in Illinois to be sampled were chosen using a random selection method. Specifically, the 205 populated areas in the state (not including the City of Chicago) were sequentially numbered and then 16 were chosen using a random number generator (Microsoft Excel). Several additional populated areas

were randomly selected in case one or more of the original 16 were not accessible for sampling.

In New York, four populated areas were selected and in the western state, six populated areas were selected for sampling based in part on their position on a randomly ranked list of populated areas in the service area of the participating electric utilities, as well as judgments about the ease of gaining permission from city officials to perform the sampling and the value of performing a study in that area for the utility.

Site Selection

Once areas were selected for sampling, road maps and USGS 7.5 minute quad(s) for each area were used to select the actual sites or properties to be sampled. The sites within each area were also selected pseudo-randomly. A coordinate system was laid out over maps of each area and a random number generator was used to select points that fell on this coordinate system. In the field, the closest accessible site to each selected grid point was sampled. Suitable sampling sites included parks, roadway medians, utility rights-of-way, commercial properties, residential properties, parking lot buffers, or vacant lots. Sites with known or suspected releases of PAHs were not sampled. In New York, 35 sites were sampled in the first populated area, 23 sites were sampled in the second populated area, 20 sites were sampled in the third populated area, and 10 sites were sampled in the fourth populated area. For Illinois and the western state, it was pre-decided that each of the 22 populated areas would have 10 sites sampled.

Sample Locations

Two locations were sampled at each site, except for two large sites in New York, where three samples were collected. At the time of sampling, the locations were selected by the field engineer to be representative of the overall site conditions based on a visual assessment of the site. The field engineer considered the area of the site, obstructions, visible evidence of contamination, and other practical matters. Samples were not collected in proximity to known sources of PAHs, such as railroad tracks or oil storage tanks.

Sample Collection and Compositing

At every location, samples were collected from both the 0 - 2.54 cm depth interval and the 2.54 - 15 cm interval. The samples were collected with pre-cleaned stainless steel trowels by marking out a one foot square area, removing any grass or ground cover, and then carefully transferring the soil from each depth interval into pre-cleaned stainless steel bowls. Each sample was briefly mixed and any rocks, glass, wood or other debris was removed before the entire sample was transferred to a pre-cleaned soil jar. No samples were collected beneath pavement, sidewalks, or other structures.

The samples were labeled, packed on ice, and shipped to the laboratory. All of the samples were composited in the laboratory as described in the following paragraphs.

The samples from 58 of the 88 sites in New York were composited by thoroughly mixing equal weights of soil from the two samples collected from 0 to 2.54 cm at each site to generate a 0 to 2.54 composite, and similarly mixing equal weights from the two samples collected from 2.54 to 15 cm to generate a 2.54 to 15 cm composite.

For the 160 Illinois samples, two types of compositing were performed. At 32 (20%) of the sites, equal portions from the two samples collected from 0 to 2.54 cm at each site were combined, as were equal portions from the two samples collected from 2.54 to 15 cm, as was done for New York. In addition, at the other 128 (80%) of the sites, the four discrete samples were composited to create one sample for the site that represented 0 to 15 cm. Specifically, 10 grams from each of the 0 to 2.54 cm samples was mixed with 50 grams from each of the 2.54 to 15 cm samples to create a composite sample representative of the interval from 0 to 15 cm.

Finally, the remaining 30 New York samples and all 60 of the western state samples were composited in the same way as the 128 Illinois samples.

Sample Analysis

Each composited soil sample was extracted by Soxhlet extraction, EPA Method 3540C. The PAHs were isolated from a portion of each extract using silica gel column chromatography (EPA Method 3630C).

The cleaned extracts were analyzed using GC/MS, EPA Method 8270 for PAHs and alkylated PAHs. In addition, the whole extracts (no cleanup) were analyzed for total hydrocarbons by GC/FID, EPA Method 8100.

Lastly, samples were analyzed for total organic carbon (TOC) using a modification (digestion with additional heat) of the Walkley-Black method (90-3).

Quality Assurance and Quality Control

A quality control plan was developed and implemented that included measures, frequencies, and criteria for calibration, blanks, spikes, replicates, and other parameters. The QC criteria were based on the analytical methods used.

The reporting limits were based on the sample equivalent of the lowest linear calibration standard. The reporting limits ranged from about 4 μg/kg to about 20 μg/kg, depending on the compound and sample conditions. Detection limits were about one half of the reporting limits and based on actual signal to noise ratios.

Data Management and Analysis

All data were checked for errors and quality control acceptability. Deviations from the data quality objectives were noted on raw data worksheets. The sample identifiers, sample descriptions, and final data were entered into a database constructed using Microsoft® Access software. All statistical and graphical analyses were conducted using the commercial software, Statistica, version 6.0, from StatSoft, Inc.

Results and Discussion

Site and Area Land Use Types

A total of 308 sites were sampled in New York, Illinois, and the western state, including a

variety of different types of sites. Based on observations made in the field, a subjective classification of the land use was made for each site sampled as part of this study. The site use classifications included recreational (23%), rights of way (40%), municipal (22%), utility (6%), open land (4%), residential (2%), conservation (1%), industrial (1%), and commercial (1%). Recreational sites included ball fields and recreational parks. Sites where a municipal right of way existed, such as the areas near streets, were designated as rights of way even if they formed part of a residential or commercial lawn. The municipal designation was used for public areas such as police stations, fire stations, and town buildings, including schools. Conservation sites included areas such as forest and nature preserves. Sites were considered utility sites either if they were owned by a utility or if there was a utility right of way in the area sampled. The residential sites were home lots or apartment complexes. Sites with businesses on them were designated as commercial for retail business, or as industrial for manufacturing or similar operations. The open land designation was used for land with no specific purpose or structures.

In addition to site use classifications, a subjective characterization of the surrounding area use was made at each of 273 sites. The resulting area use classifications included heavy residential (52%), commercial (20%), light industrial (11%), light residential (10%), agricultural (2%), heavy industrial (1%), and rural (3%). Areas were considered heavy residential if houses were present at a density of at least one house per acre. Otherwise, if the houses were sparse, the area was assigned the light residential designation. Similarly, areas with a high density of non-retail businesses were considered heavy industrial, particularly if manufacturing was present. On the other hand, areas with just one or a few non-retail businesses were considered light industrial. Commercial was used to describe areas with retail businesses. For sites bordering farmland, the area was considered agricultural. Lastly, areas with very few businesses or residences, and without farmland, were designated as rural.

Summary of Physical Sample Characteristics

Consistent with the intent of the sampling plan, the samples contained various amounts of silt, sand, clay and gravel. For the 218 samples classified, the TOC levels ranged from 0.2% to 17% with a median TOC of 2.5%. The percent solids content was generally 80 to 95%.

Sample Results for PAHs

For this paper, six PAH compounds were chosen to illustrate the PAH data.. The six compounds spanned the range of molecular weight, and environmental transport, fate, and toxicity properties. Table 1 summarizes the PAH results for all 308 samples.

Summary Statistics for PAH Results from All Sites

A working data set was generated for the statistical and graphical analyses reported in this paper. The data set was generated in two ways. First, one half the sample-specific detection limit was substituted for non-detects. Then, arithmetic composites were generated where the 0 to 2.54 cm and 2.54 to 15 cm samples were analyzed separately. This was done by generating weighted averages based on the sampling intervals, which are representative of the 0 to 15 cm interval at those locations.

Table 1. Summary Statistics for All 308 Samples (ug/kg)

Compound	Range	Mean	Median
naphthalene	ND – 2,850	59	19
pyrene	ND – 16,800	540	140
benz(a)anthracene	ND – 9,120	311	69
benzo(a)pyrene	ND – 11,700	367	87
dibenz(a,h)anthracene	ND – 3,010	95	22
indeno(1,2,3-cd)pyrene	ND – 8,240	272	63

Table 1 and Table 2 list the summary description statistics for all 308 samples. Included in the statistics for each compound are the mean, median, range, upper and lower quartiles, and 5th and 95th percentiles. All statistics reported in Tables 1 and 2 were performed on the raw data, assuming that the concentrations of each variable (PAH analyte) are normally distributed. As shown in Table 1, benzo(a)pyrene concentrations ranged from ND to 11,700 µg/kg with a median concentration of 87 µg/kg. The upper quartile concentration was 303 µg/kg, while the upper 95th percentile concentration was 1,590 µg/kg. These concentrations appear to be consistent with literature-reported levels for anthropogenic background in small to medium-sized residential, commercial, and light industrial areas, but notably lower than background observed in more highly populated cities and commercial/industrial areas (Bradley et al., 1994 and MA DEP, 2002).

Table 2. Other Summary Statistics for All 308 Samples (ug/kg)

Compound	Lower Quartile	Upper Quartile	5th Percentile	95th Percentile
naphthalene	8	48	3.9	190
pyrene	44	440	5.9	2,280
benz(a)anthracene	19	256	3.9	1,410
benzo(a)pyrene	29	303	4.6	1,590
dibenz(a,h)anthracene	10	74	4.9	440
indeno(1,2,3-cd)pyrene	19	223	9.2	1,250

The differences between the mean concentrations and the median concentrations strongly suggest that the data are not normally distributed. This observation was explored further using normal probability plots and frequency histograms. Figures 2 and 1 show normal probability plots and frequency histograms for benzo(a)pyrene that clearly indicate the lognormal distribution of the data for those analytes. Similar plots were developed for the other analytes with similar results, but are not included in this paper.

Figures 3 and 4 show the normal probability plots and frequency histograms for the log-transformed concentration data of benzo(a)pyrene. In contrast to the raw concentration data, the log-transformed data are clearly normally distributed.

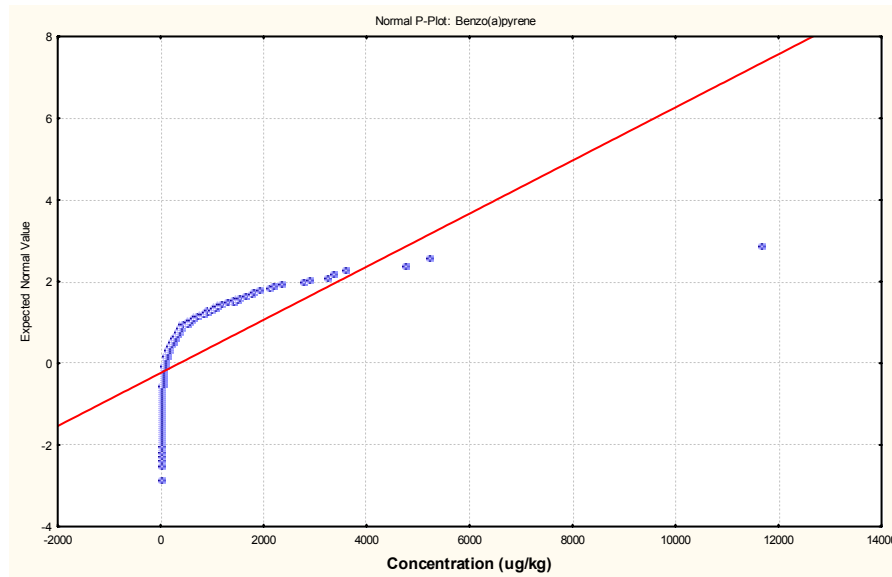**Figure 1. Normal Probability Plot for Benzo(a)pyrene – 308 Samples**

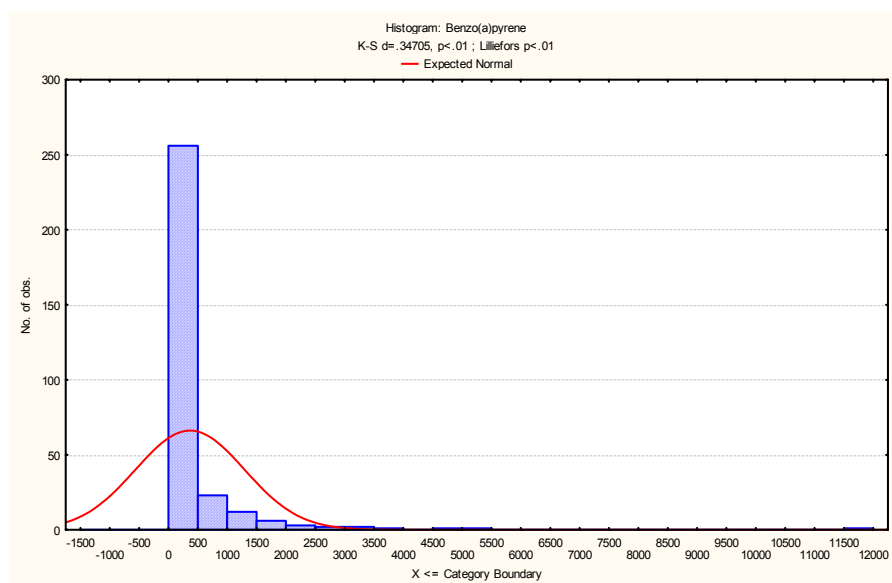**Figure 2. Normal Histogram Plot for Benzo(a)pyrene – 308 Samples**

Figure 3. Lognormal Probability Plot for Benzo(a)pyrene – 308 Samples
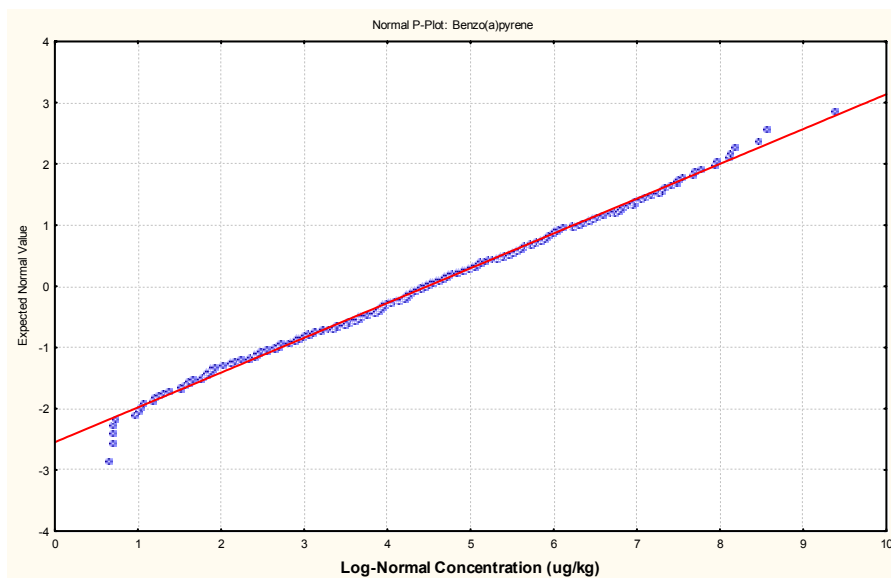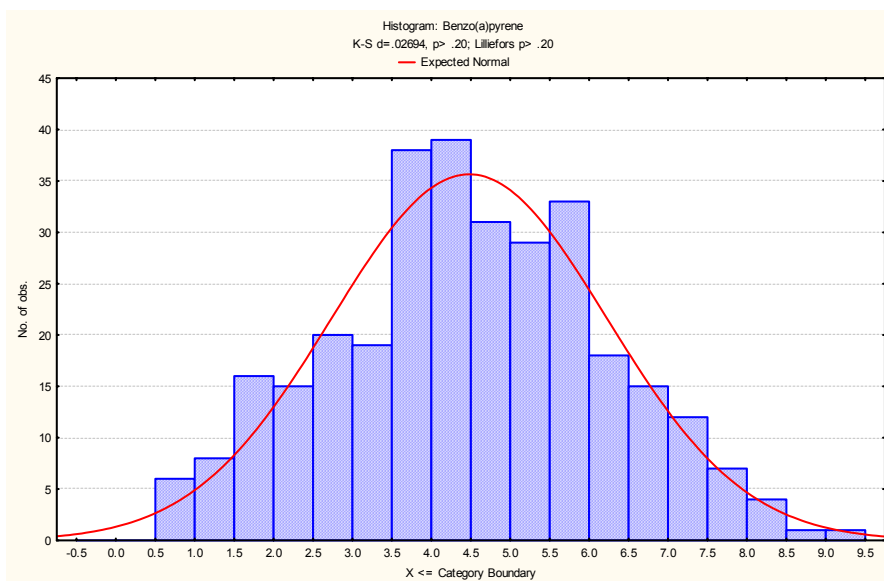

Figure 4. Lognormal Histogram Plot for Benzo(a)pyrene – 308. Samples

The concentrations of PAHs were compared to U.S. EPA residential risk-based concentrations (RBCs) and a substantial number of samples exceeded the RBCs. As shown in Table 3, 50% of the 308 samples collected had benzo(a)pyrene concentrations that exceeded the residential RBC. Clearly, cleanup criteria based on residential RBCs for PAHs would be difficult to implement in any urban setting. If the 95% percentile of this data set is used to set cleanup criteria, the

concentrations shown in Table 4 result for several PAHs

Table 3. Exceedances of EPA Residential Risk-Based Concentrations

	EPA RBC	Exceedances	% Exceedances
Benz(a)anthracene	870	28/308	9
Benzo(a)pyrene	87	154/308	50
Dibenz(a,h)anthracene	87	69/308	22
Indeno(1,2,3-cd)pyrene	870	26/308	8

Table 4. 95th Percentiles for PAHs by State

Compound	Chicago[1]	New York	Illinois	Western State	EPA RBC[2]
naphthalene	306	219	133	139	
pyrene	18,400	4,610	1,710	672	
benz(a)anthracene	11,100	2,790	1,060	205	870
benzo(a)pyrene	11,600	3,220	1,260	262	87
dibenz(a,h)anthracene	1,040	707	193	61	87
indeno(1,2,3-cd)pyrene	5,890	2,250	704	206	870
N=	56	88	160	60	

1 Polynuclear Aromatic Hydrocarbon Background Study, City of Chicago, IL: n = 56

2 risk-based concentrations

Summary Statistics for PAH Results by Site and Area Uses

Benzo(a) pyrene was used to illustrate the distribution of PAHs by site and area use. Tables 5 and 6 show the results. The data do not show a clear trend by site use (Table 5). However, the data suggest that PAH concentrations are higher in areas that are industrial or commercial regardless of the land use of the individual site sampled. It is important to note, however, that the number of samples analyzed in several site use and area use categories is very small, and that the data may not be representative of those areas generally. For example, only one sample out of 308 was collected on an actual commercial site, whereas 72 samples were collected in commercial areas. The data suggest that the one commercial site result is not representative of commercial sites generally.

Table 5. Summary Statistics by Site Uses for Benzo(a)pyrene

	N	Median (ug/kg)	Range (ug/kg)
Rights of Way	123	72	2.1 – 3,260
Recreational	72	100	2.6 – 2,360
Municipal	69	100	2.0 – 11,600
Utility	18	33	2.0 – 2,190
Open Land	12	130	2.8 – 1,820
Residential	7	86	30 – 510
Conservation	4	180	6.7 – 4,740
Industrial	2	190	70 – 310
Commercial	1	1.9	1.9 – 1.9

N = 308; results based on 0 – 15 cm interval and ND set to ½ EDL.

Table 6. Summary Statistics by Area Uses for Benzo(a)pyrene

	N	Median (ug/kg)	Range (ug/kg)
Heavy Residential	123	68	2.0 – 5,210
Commercial	72	110	1.9 – 3,360
Light Industrial	69	94	2.7 – 2,770
Light Residential	18	26	2.0 - 870
Rural	12	45	6.4 – 4,740
Agricultural	7	68	3.3 - 140
Heavy Industrial	4	1,020	303 – 2,190

N = 273; results based on 0 to 15 cm interval; ND set to ½ EDL

Comparison of This Study to Other Background PAH Studies

As discussed previously, several studies of PAH concentrations in urban background have been reported in the literature. For example, as part of the reconstruction of the central artery, Massachusetts Department of Environmental Protection (MADEP) analyzed hundreds of soil samples for PAHs. The samples were collected in downtown Boston at various depths, primarily in filled land. In another study, the Massachusetts LSPA compiled the results of "background" soil samples from site investigation reports on file at the MADEP. While not collected as part of a single, controlled study, the data were considered representative of urban background. Table 7 shows the benzo(a)pyrene results extracted from several investigations of PAHs in urban background. The data are generally higher than those collected by META; likely because of a higher proportion of samples collected from larger urban areas (e.g., Boston) and because more

samples were collected from sites impacted by known PAH sources and urban fill. This is also evident in Table 6 where the benzo(a)pyrene concentrations in the City of Chicago are generally higher than other populated areas in the State of Illinois.

Table 7. Summary Statistics for Benzo(a)pyrene in Urban Soil from Several Studies (ug/kg)

Data Set	N	Range	Mean	Median	95th Percentile
CA/T Project	873	31 – 230,000	NA	300	17,000
LSPA Project	489	ND – 222,000	NA	440	NA
Watertown	17	600 – 6,080	NA	NA	4,770
Med City/Mill Brook	67	ND – 9,700	NA	NA	3,300
ENSR – Urban Soils	62	ND – 13,000	1,320	NA	NA

Conclusions

A controlled study of the concentrations of PAHs in 308 urban surface soil samples indicated that PAHs are present in nearly all surface soils. Specifically:

- The concentrations of PAHs in urban surface soil is lognormally distributed.

- The concentrations of high molecular weight PAHs are generally much higher than low molecular weight PAHs.

- 50% of the sites sampled exceeded the residential RBC for benzo(a)pyrene.

- For the samples analyzed in this study, there appears to be little difference in PAH concentrations by site use; however, samples collected in industrial and commercial areas have higher PAH concentrations than those collected in residential areas.

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